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THE IMPROVEMENTS IN PEAK RESOLUTION AND IN REPRODUCIBILITY OF SPECTROCHRONOGRAMS OF DIFFERENT SULPHUR FORMS IN COALS BY ADDITION OF SILICA (SiO_2) POWDER TO COAL SAMPLE

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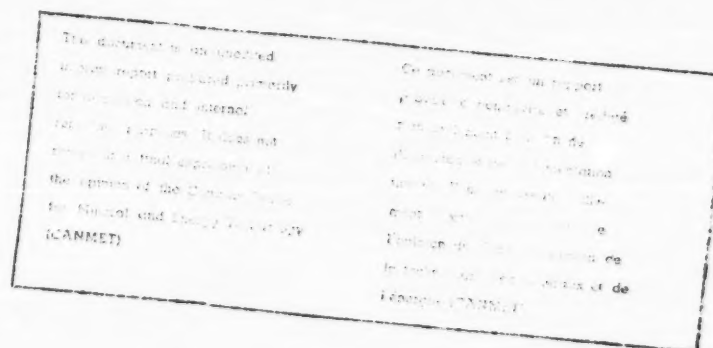
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and

Louis L. Sirois**

ABSTRACT

A new sample preparation technique was developed for the CANMET SULPHUR FORM ANALYSER. Initially the spectrochronograms of different sulphur forms in coals suffered from poor resolution as well as from poor reproducibility of different sulphur peaks. Thorough mixing of inert silica (SiO_2) powder (100% -60 μm) with coal samples followed by regular analysis dramatically improved the resolution as well as the reproducibility. Silica-to-coal ratios from 5:1 to 10:1 by weight were found to be optimal for good resolution and reproducibility.

Keywords : High Sulphur Coal, Coal Analyser, Sulphur in Coal,
CANMET Sulphur Form Analyser, Silica-Coal Mixture

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ADDITION DE POUDRE DE SILICE (SiO_2) À L'ÉCHANTILLON
DE CHARBON POUR AMÉLIORER LA RÉOLUTION DE POINTE ET LA
REPRODUCTIBILITÉ DES SPECTROCHRONOGRAMMES DES DIFFÉRENTES
VARIÉTÉS DE SOUFRE DANS LES CHARBONS

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et

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RÉSUMÉ

Une technique nouvelle de préparation des échantillons au moyen de L'ANALYSEUR DES VARIÉTÉS DE SOUFRE MIS AU POINT PAR CANMET a été développée. Au début, la résolution des spectrochronogrammes des diverses variétés de soufre dans les charbons était faible et la reproductibilité des différentes crêtes, peu élevée. En mélangeant à fond la poudre de silice (SiO_2), (100% -60 m) et les échantillons de charbon avant l'analyse régulière, il a été possible d'améliorer, de façon remarquable, la résolution et la reproductibilité. Les rapports silice-charbon de 5:1 à 10:1 (par poids) se sont avérés idéals pour obtenir une résolution et une reproductibilité adéquates.

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INTRODUCTION

The surface chemistry laboratory in MPL/MSL/CANMET has developed a unique technique for the quantitative analysis of different sulphur forms in coals. The method utilizes the difference in the evolution kinetics of SO_x from different sulphur forms in coal. The analysis technique was described by Kwang S. Moon and Louis L. Sirois(1) and patents are pending in Canada(2) and in the U.S.A.(3). Recognizing the world-wide impact of the development of such a instrument, CANMET has been developing a prototype "CANMET SULPHUR FORM ANALYZER" based on the technique.

During the initial development phase, however, a great deal of difficulty was encountered in reproducing spectrochronograms for actual coal sample(4). It was later realized that the erratically high local temperature might be responsible for the poor reproducibility and poor resolution of the spectrochronograms. In order to improve the reproducibility of the spectrochronograms for actual coals, the control of the local temperature was attempted by mixing the coal samples with different solid matrix materials, e.g. silica, titania, alumina, clay, salts and cabonates.

EXPERIMENTAL RESULTS AND DISCUSSION

The initial difficulties encountered in reproducing spectrochronograms for different sulphur forms of actual coal samples are indicated in Figure 1. The reproducibility was very poor, making the deconvolution of different sulphur peaks virtually impossible. In order to improve the reproducibility of the spectrochronograms for actual coals, the erratic fluctuation of the local reaction temperature was controlled by the mixing of coal samples with different solid matrix materials, e.g. silica, titania, alumina, clay, salts and cabonates. As expected, silica and titania were found to be inert. They gave no side reaction with sulphur resulting in the correct total sulphur analysis. However, titania sample used enhanced the evolution kinetics of SO_x rather than slowing

down, making the analysis more difficult. Other oxides and silicate clay materials that contain elements which react with sulphur were found to be inadequate for the purpose. As was the case with the coal samples, silica has to be ground very fine prior to mixing. Coal and silica powders have to be mixed thoroughly for good results. The reproducibility of spectrochronograms was improved as the ratio of silica to coal was increased from 2:1 to 20:1. However, very good resolution between different sulphur peaks was obtained at silica-to-coal ratio of 5 to 10:1. Increasing the content of silica beyond this level generally resulted in the broadening of all peaks of the spectrochronograms, allowing the use of high temperature in the reaction chamber.

Six different coal samples were analysed in duplicate with and without addition of silica matrix material; 100 mg of coal was mixed with 900 mg of silica for each study. The silica (SiO_2) used was very fine, i.e. 100% -60 μm . In all cases, the sulphur content was the same, independent of the presence of silica (Table 1).

The dramatic improvements in the resolution of peaks and in the reproducibility of spectrochronograms by addition of silica to a coal sample can be seen in Figures 1 and 2 in the absence and in the presence of silica, respectively. In this study 900 mg of silica and 100 mg of a coal sample was analysed together at 525°C. In a ten replicate study of another coal of 100 mg with 900 mg of silica addition at 500°C, an excellent reproducibility in the sulphur content, peak position and height for the primary and the secondary peaks was obtained (Table 2 and Figure 3). After ten replications, the total sulphur content of the coal sample was found to be $4.22 \pm 0.07\%$. The primary peak of 50.0 ± 7.1 nm occurred at 261 ± 4 seconds, while the secondary peak of 18.8 ± 1.1 nm appeared at 113 ± 3 seconds. Figure 4 shows the duplicate spectrochronograms for five different coal samples containing varying amounts of different sulphur forms. The resolution of different peaks corresponding to the different sulphur forms is very good. The reproducibility for different coals is also considered very good.

Table 1 : Total Sulphur Analysis of Different Coals,
at 525°C With and Without Silica Addition

Coal Sample Number	% Total Sulphur		Relative Difference (%)
	Coal(100 mg) only	Coal(100 mg)+Silica(900 mg)	
1	0.66 ± 0.02	0.67 ± 0.01	+ 1.5
3	1.01 ± 0.01	1.01 ± 0.01	± 0.0
5	2.12 ± 0.02	2.14 ± 0.02	+ 0.9
6	2.44 ± 0.05	2.43 ± 0.02	- 0.4
7	3.58 ± 0.01	3.61 ± 0.05	+ 0.8
8	4.54 ± 0.01	4.55 ± 0.01	+ 0.2

Table 2 : Reproducibility of Total Sulphur Content, Peak Time
and Peak Height for the Primary and Secondary Peaks
of IR SO_x Spectrochronograms of the Same Coal

Replicate Number	Total Sulphur Content(%)	Secondary Peak		Primary Peak	
		Time(sec)	Height(mm)	Time(sec)	Height(mm)
1	4.27	110	19.0	258	51.5
2	4.12	115	17.0	269	42.0
3	4.24	115	18.0	264	50.5
4	4.14	115	17.5	263	43.5
5	4.18	109	18.5	259	45.5
6	4.22	115	18.5	262	49.0
7	4.18	115	18.5	262	45.0
8	4.22	108	19.5	259	48.5
9	4.37	113	21.0	252	67.0
10	4.30	110	20.0	258	57.5
$\bar{X} \pm S(*)$	4.22 ± 0.07	113 ± 3	18.8 ± 1.1	261 ± 4	50.0 ± 7.1

* Mean ± Standard Deviation for ten replicates.

To study the effect of reaction temperature on the shape of the spectrochronograms, 100 mg of a coal sample was mixed with 900 mg of silica powder and analysed at 500, 525, 550, 600 and 700°C (Figure 5). As the reaction temperature increased from 500 to 700°C, the intensity of the primary and the secondary peaks grew from 43.5 to 141.0 mm and from 17.0 to about 40.0 mm, respectively. On the other hand, the peak position shifted from 264 to 84 seconds for the primary peak and from 114 to about 48 seconds for the secondary peak (Table 3 and Figure 6). The changes in peak height and position were more pronounced for the primary peak than for the secondary one. As the reaction temperature increased, the resolution between the primary and the secondary peaks became progressively worse (Figure 5). Since the same sample was used for each temperature, the area under the IR SO_x spectrochronograms remained unchanged, indicating that the total sulphur content was identical for all cases. This was made possible by the simultaneous changes in the peak heights and in the peak positions of the spectrochronograms.

ACKNOWLEDGEMENT

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Table 3 : Changes in Peak Positions and in Peak Heights of IR SO_x
Spectrochronograms of Coal (100 mg) and Silica (900 mg)
Mixture at Different Reaction Temperatures

Reaction Temp. (°C)	Primary Peak		Secondary Peak	
	Time(sec)	Height(mm)	Time(sec)	Height(mm)
500	264	43.5	114	17.0
525	201	71.0	99	22.5
550	185	83.0	95	24.0
600	131	111.5	72	30.0
700	84	141.0	48(?)	40.0(?)

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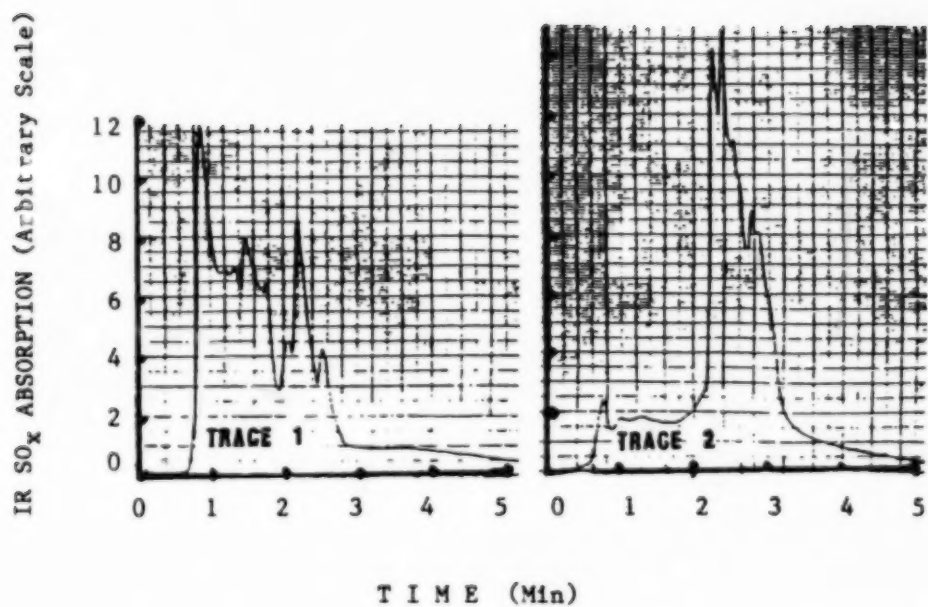


Figure 1 : Duplicate Spectrochronograms for a Coal Sample (100 mg)
without Silica at 525°C

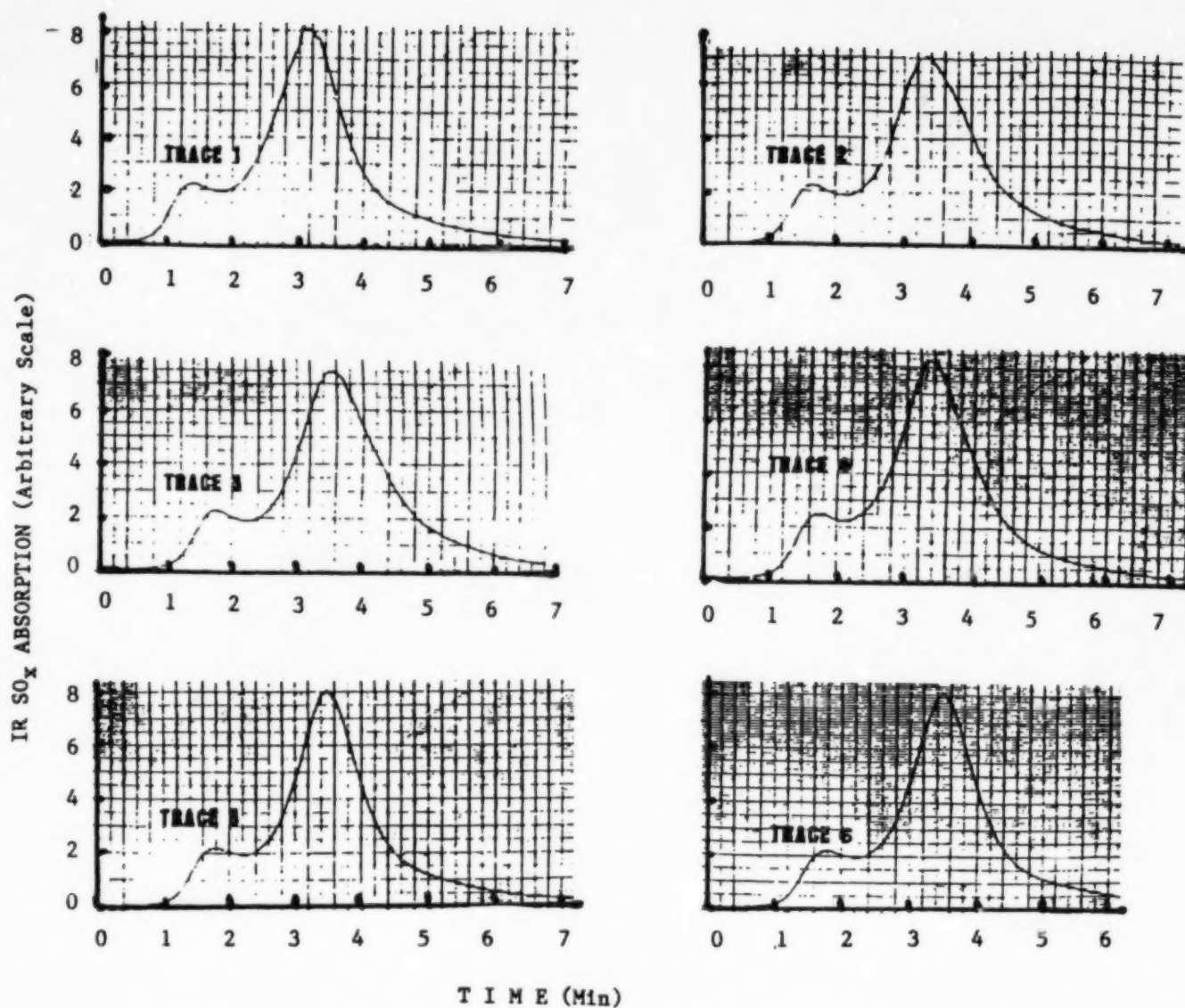


Figure 2 : Six Replicate Spectrochronograms for a Coal Sample (100 mg) with Silica (900 mg) at 525°C

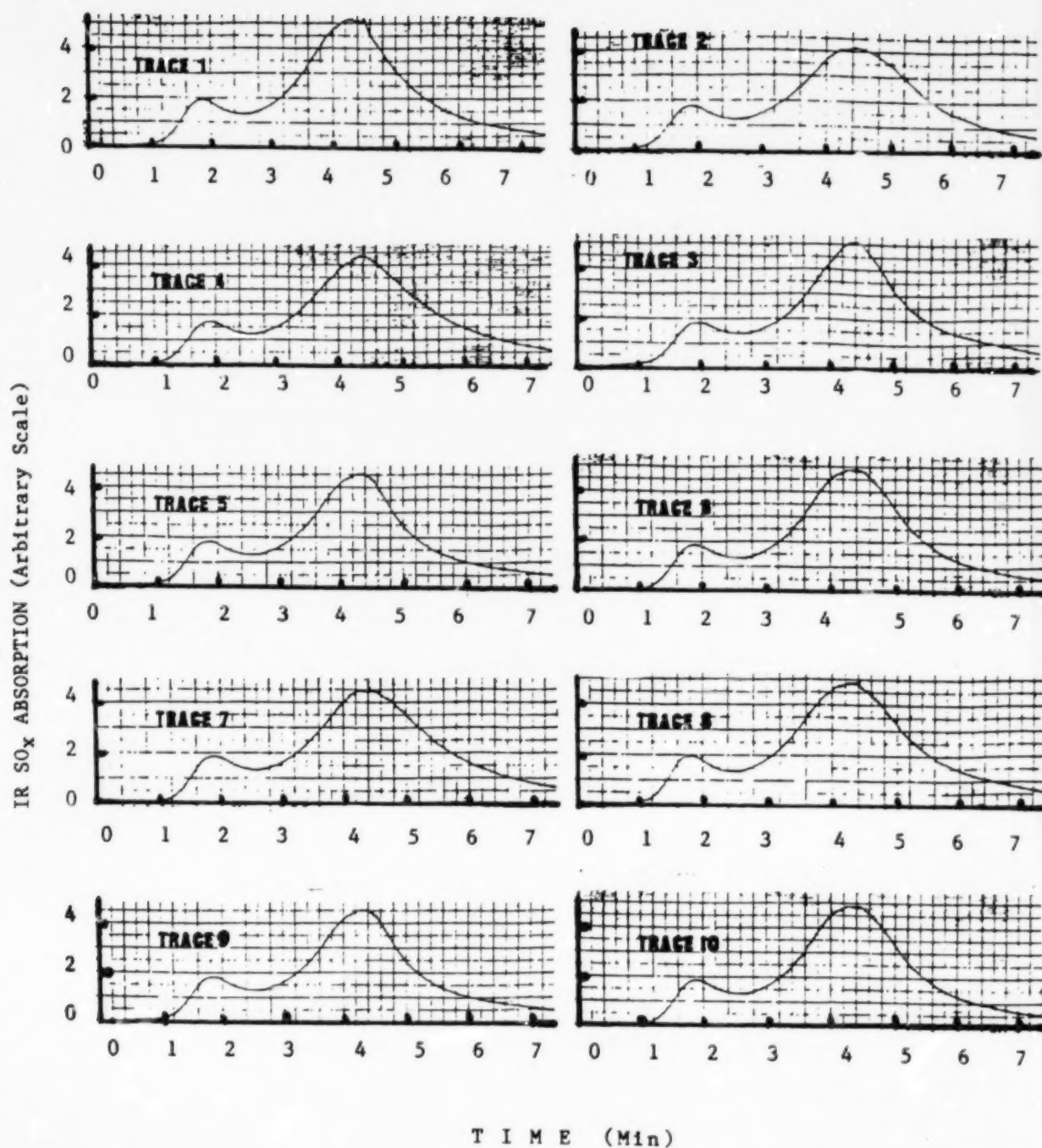


Figure 3 : Ten Replicate Spectrochronograms for a Coal Sample (100 mg)
with Silica (900 mg) at 500°C

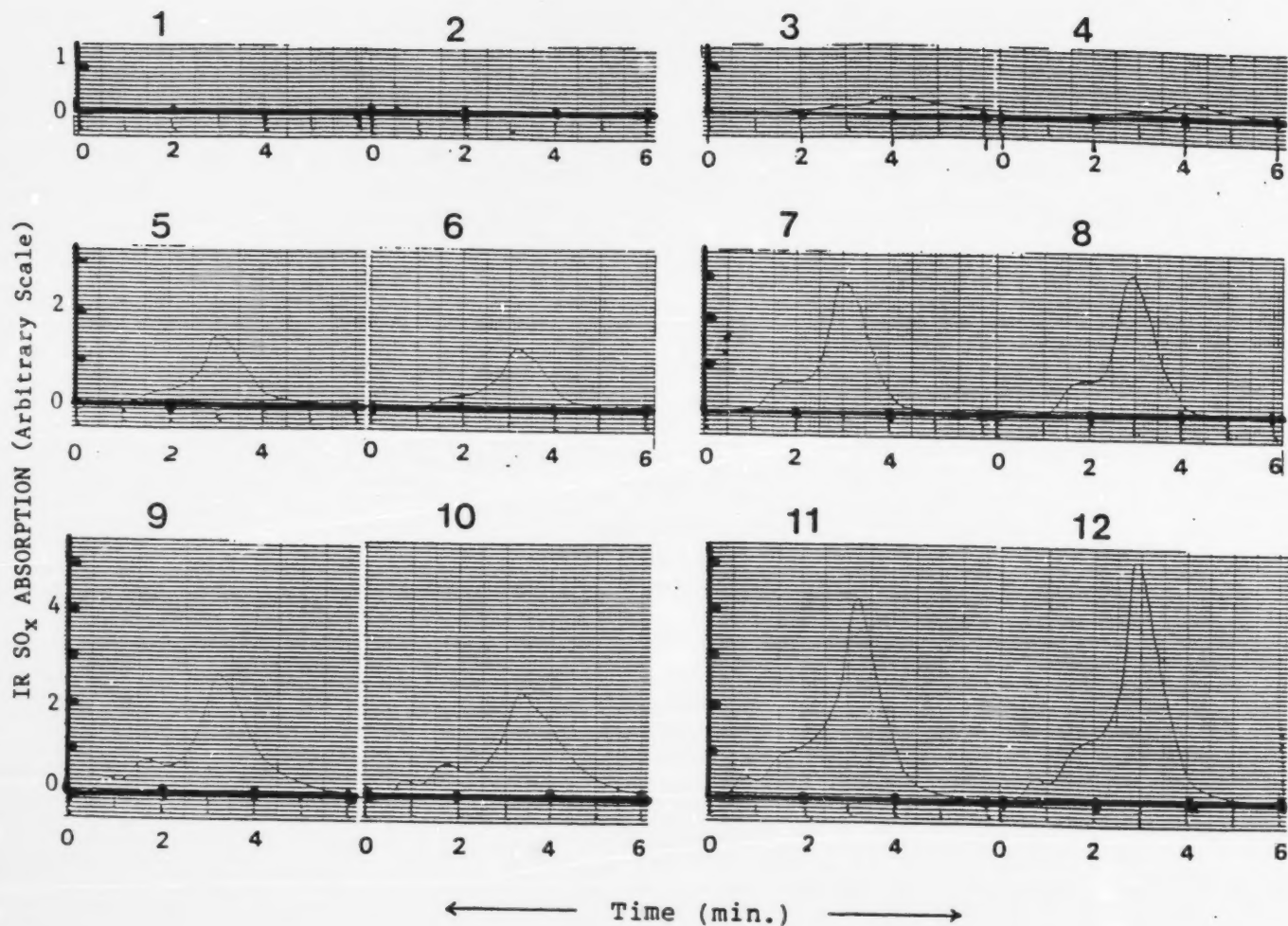


Figure 4 : Duplicate Spectrochronograms for five Coal Samples (100 mg)
with Silica (900 mg) at 550°C

LEGEND:	Trace No.	Sample No.	% Sulphur Forms			
			Organic	Pyritic	Sulphatic	Total
	1 & 2	Silica only	0.00	0.00	0.00	0.00
	3 & 4	Coal S-1	0.42	0.03	0.06	0.51
	5 & 6	Coal S-2	0.71	0.38	0.02	1.11
	7 & 8	Coal S-3	0.73	1.42	0.10	2.25
	9 & 10	Coal S-4	1.18	1.00	0.73	2.91
	11 & 12	Coal S-5	1.36	2.09	0.66	4.11

IR SO_x ABSORPTION (Arbitrary Scale)

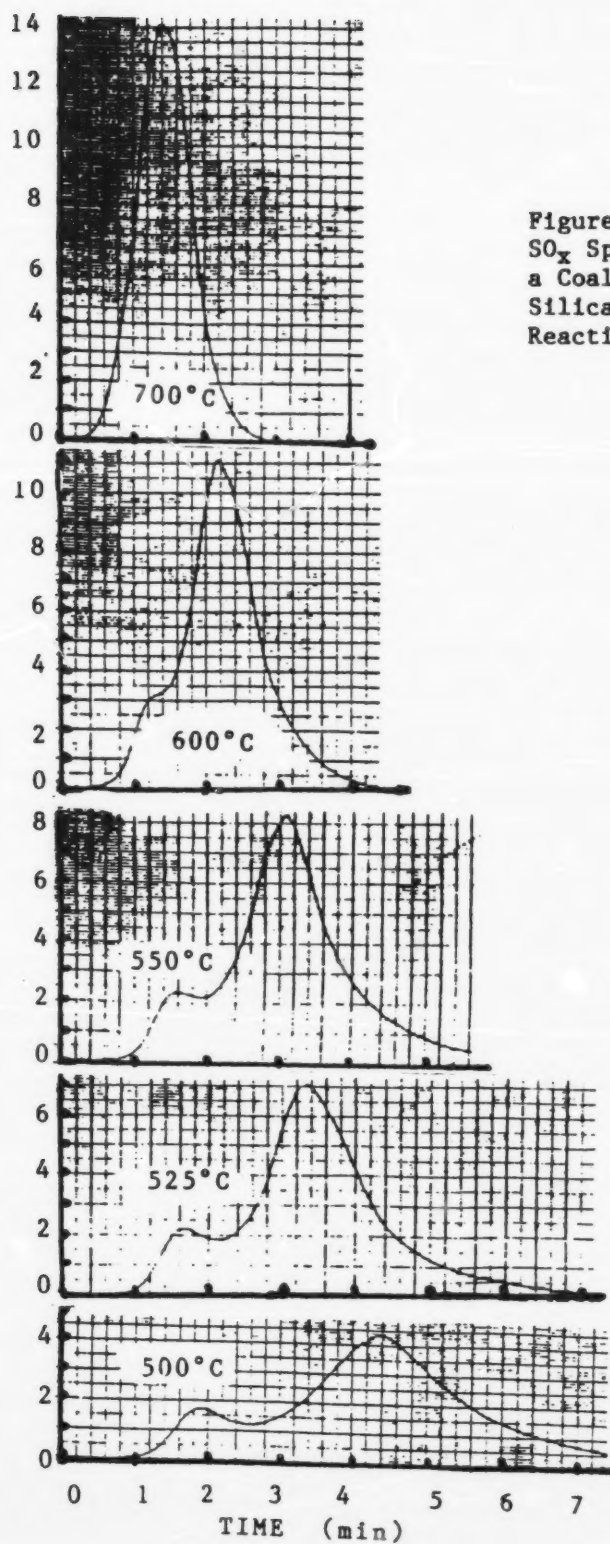


Figure 5 :
SO_x Spectrochronograms for
a Coal Sample (100 mg) with
Silica (900 mg) at Different
Reaction Temperatures (°C)

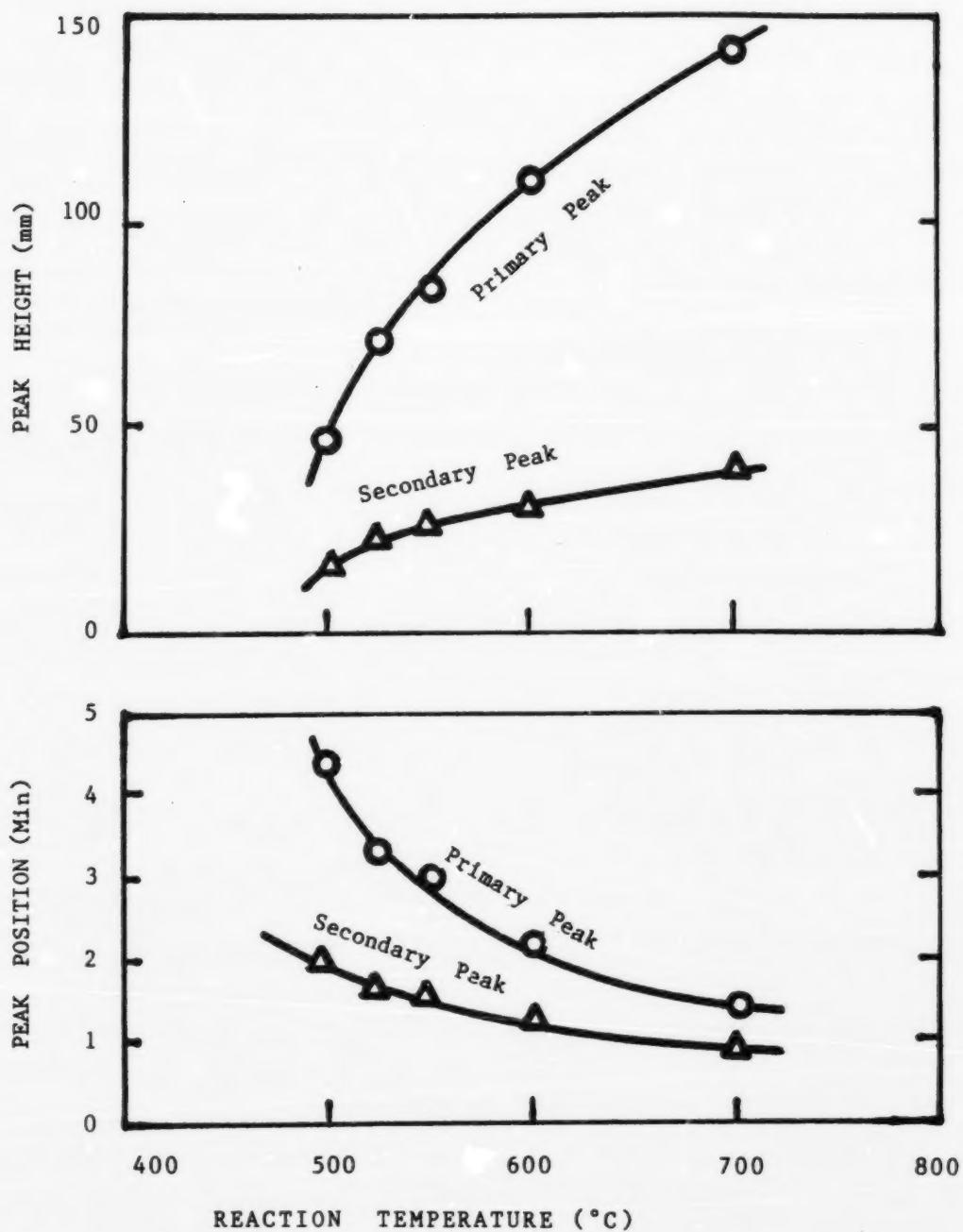


Figure 6 : Changes in Peak Height (mm) and in Peak Position (Min) for the Primary and the Secondary Peak of SO_x Spectrochronograms of a Coal Sample (100 mg) with Silica (900 mg) at Different Reaction Temperatures ($^{\circ}\text{C}$)